

Distillation Theory and Its Application to Optimal Design of Separation Units

F. B. Petlyuk



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Phase Equilibrium and Its Geometric Presentation

1.1. Introduction

The process of distillation can be presented as consisting of numerous states of phase equilibrium between flows of liquid and vapor that have different compositions. Geometric analysis of the distillation process represented in the so-called *concentration space* (C) is the main instrument for understanding its regularities.

That is why, before we start the examination of the existing distillation process and its geometric interpretation, it is necessary to consider geometric interpretation, of the phase equilibrium. Numerous methods of calculating phase equilibrium are described in many monographs and manuals (see, e.g., Walas [1985]).

We will not repeat these descriptions but instead will examine only representation of equilibrium states and processes in concentration space.

1.2. Concentration Space

Molar composition of an n -component mixture is presented as an array that holds molar concentrations of all components:

$$x_i = \frac{m_i}{\sum m_i} \quad (1.1)$$

$$\sum x_i = 1 \quad (1.2)$$

where m_i is the amount of moles of the component i in the mixture.

Concentration space of an n -component mixture C_n is a space in which every point corresponds to a mixture of definite composition. *Dimensionality* of concentration space corresponds to the number of concentrations of components that can be fixed independently.

The $(n - 1)$ concentration for an n -component mixture can be fixed independently because concentration of the n th component can be found from Eq. (1.2). That is why the dimensionality of the concentration space of binary mixture C_2 is one, of ternary mixture C_3 – two, of four-component mixture C_4 – three, etc.

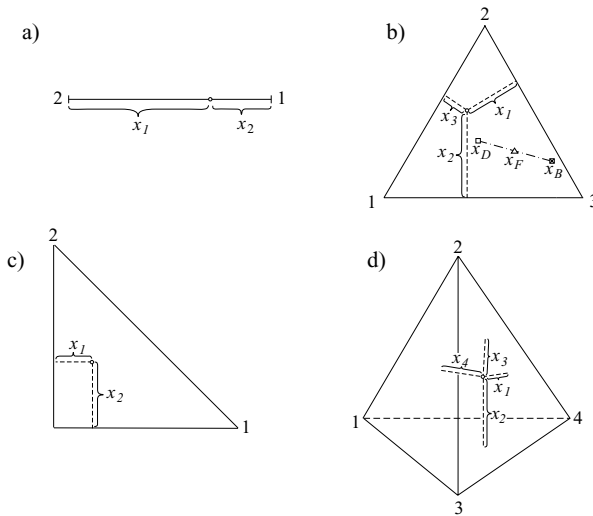


Figure 1.1. Concentration simplexes (a) for binary mixtures, (b, c) for three-component mixtures, and (d) for four-component mixtures. x_1, x_2, x_3, x_4 , concentrations of components.

Concentration space is the number of points representing all possible compositions of an n -component mixture. Concentration space of a binary mixture C_2 is a segment of unit length; the ends correspond to pure components, and the inner points correspond to mixtures of various compositions (Fig. 1.1a)

For a three-component mixture, it is convenient to present the composition space C_3 as an equilateral triangle, the height of which equals one (Fig. 1.1b). The triangle's vertexes represent pure components, the points within its sides, represent the binary constituents of the three-component mixture, and the inner points of triangle represent the three-component mixture compositions. The lengths of the perpendiculars to the triangle's sides correspond to the concentrations of the components indicated by the opposite vertexes. The described system of coordinates, which bears the name of the system of uniform coordinates, was introduced by Mobius and was further developed by Gibbs.

Another way to present a three-component mixture's composition space C_3 implies the use of an isosceles right-angle triangle (Fig. 1.1c), with a side equal to one. In this method of representation the concentrations of components 1 and 2 are expressed by the length of perpendicular segments, as in the first case of the composition's representation, and the concentration of the third component is defined in accordance with the formula: $x_3 = 1 - (x_1 + x_2)$.

Four-component mixture composition can be represented by a point of an equilateral tetrahedron C_4 (Fig. 1.1d). In this tetrahedron the vertexes represent the pure components, the edges represent the binary constituents, and the faces represent the three-component constituents.

In this book, we will often represent the mixture compositions corresponding to the material balance (e.g., the compositions of feed flow and product flow of

the distillation column):

$$Fx_{iF} = Dx_{iD} + Bx_{iB} \quad (1.3)$$

$$(D + B)x_{iF} = Dx_{iD} + Bx_{iB} \quad (1.4)$$

$$D(x_{iF} - x_{iD}) = B(x_{iB} - x_{iF}) \quad (1.5)$$

Equation (1.5) represents the so-called *lever rule*: points x_{iF} , x_{iD} , and x_{iB} are located on one straight line, and the lengths of the segments $[x_{iF}, x_{iD}]$ and $[x_{iB}, x_{iF}]$ are inversely proportional to the flow rates D and B (Fig. 1.1b). Mixture with a component number $n \geq 5$ cannot be represented clearly. However, we will apply the terms simplex of dimensionality $(n - 1)$ for a concentration space of n -component mixture C_n , hyperfaces C_{n-1} of this simplex for $(n - 1)$ -component constituents of this mixture, etc.

1.3. Phase Equilibrium of Binary Mixtures

An equilibrium between liquid and vapor is usually described as follows:

$$y_i = K_i x_i \quad (1.6)$$

where y_i and x_i are equilibrium compositions of vapor and liquid, respectively, and K_i is the liquid–vapor phase equilibrium coefficient.

To understand the mutual behavior of the components depending on the degree of the mixture's nonideality caused by the difference in the components' molecular properties, it is better to use graphs $y_1 - x_1$, $T - x_1$, $T - y_1$, $K_1 - x_1$, and $K_2 - x_1$ (Fig. 1.2). In Fig. 1.2, the degree of nonideality increases from a to h : a is an ideal mixture, b is a nonideal mixture with an *inflection on the curve* $y_1 - x_1$ (a and b are zeotropic mixtures), c is a mixture with a so-called *tangential azeotrope* (curve $y_1 - x_1$ touches the diagonal in the point $x_1 = 1$), d is an *azeotropic mixture* with minimum temperature, e is a mixture with a so-called *inner tangential azeotrope*, f is a *mixture with two azeotropes*, g is a *heteroazeotropic mixture*, and h is an *azeotropic mixture with two liquid phases*. *Azeotrope* is a binary or multicomponent mixture composition for which the values of phase equilibrium coefficients for all components are equal to one:

$$K_i^{Az} = 1 \quad (i = 1, 2, \dots, n) \quad (1.7)$$

Heteroazeotrope is an overall composition of a mixture with two liquid phases for which the values of the overall coefficients of phase equilibrium for all components are equal to one:

$$K_{ov,i}^{Haz} = 1 \quad (i = 1, 2, \dots, n) \quad (1.8)$$

where $K_{ov,i} = y_i / x_{ov,i}$, $x_{ov,i} = x_i^{(1)}a + x_i^{(2)}(1 - a)$, a is the portion of the first liquid phase in the whole liquid, and $x_i^{(1)}$ and $x_i^{(2)}$ are the concentrations of the i th component in first and second liquid phases correspondingly.

In this book, we will see that the previously discussed features are of great importance. Even b case results in serious abnormalities of the distillation process.

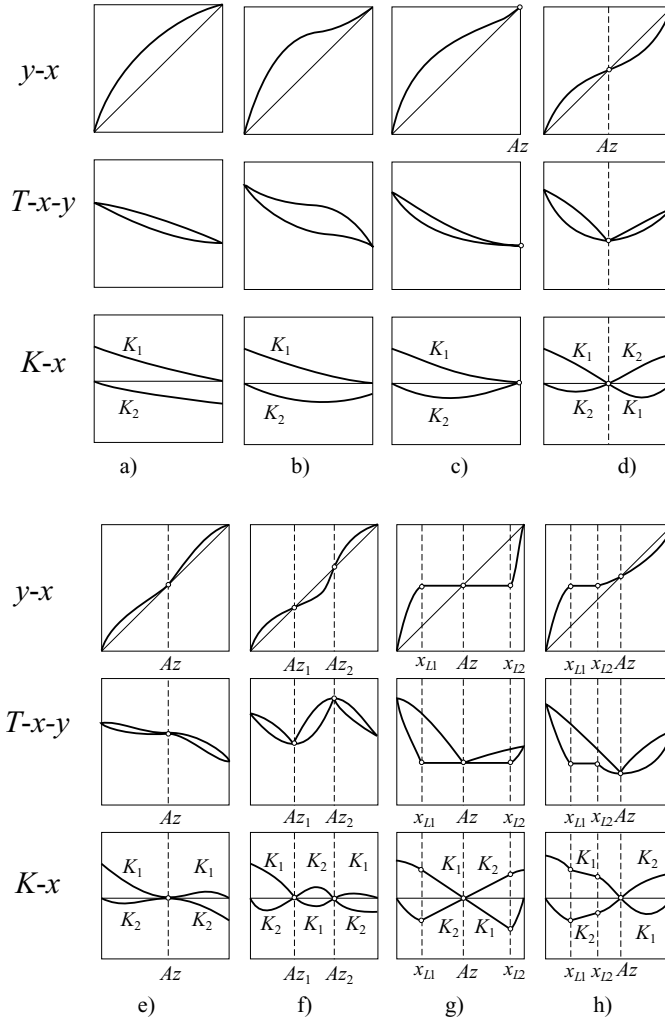


Figure 1.2. Phase equilibrium of binary mixtures: (a) ideal mixture; (b) nonideal mixture; (c) tangential azeotropic mixture ($x_1, Az = 1$); (d) azeotropic mixture; (e) mixture with internal tangential azeotrope ($0 < x_1, Az < 1$); (f) mixture with two azeotropes Az_1 and Az_2 ; (g) heteroazeotropic mixture; and (h) azeotropic mixture with two liquid phases ($y - x$, $T - x - y$, and $K - x$ diagrams). Az , azeotropic or heteroazeotropic point; x_{L1} and x_{L2} , compositions of liquid phases.

The appearance of azeotropes makes the separation of the mixture into pure components impossible without special procedure application.

Further increase in nonideality and transition to heteroazeotropes makes it again possible to separate mixtures, not using just a distillation column, but a *column with decanter* complex. Cases *e* and *f* occur, but very seldom; therefore, we will not consider them further.

In the azeotrope point, $K_1 = K_2 = 1$. For a *tangential azeotrope*, $x_1^{Az} = 1$ or $x_1^{Az} = 0$. It might seem that a tangential azeotrope is no obstacle for separation.

However, later in this book, we will see that if $x_1^{Az} = 1$, it is impossible to get component 1 with a high degree of purity, and if $x_1^{Az} = 0$, it is impossible to get component 2 with a high degree of purity.

I.4. Phase Diagrams of Three-Component Mixtures

Three-component mixtures represent the simplest type of multicomponent mixtures. The majority of multicomponent mixture peculiarities become apparent in three-component mixtures. This is why the three-component mixtures are best studied. Liquid–vapor equilibrium in the concentration triangle C_3 is represented by a vector connecting a point of liquid composition with a point of equilibrium vapor composition $x \rightarrow y$. This vector is called a *liquid–vapor tie-line*. The opposite vector $y \rightarrow x$ (vapor–liquid) is called a *vapor–liquid tie-line*. The tie-lines field in the concentration triangle characterizes phase equilibrium in each of its points.

However, tie-lines can cross each other. That is why, for phase equilibrium characteristics in the concentration space, it is convenient to use another kind of line, the so-called *residue curves*. Let's consider a process of *open evaporation* (*simple distillation*) illustrated in Fig. 1.3.

Let's assume that the initial amount of liquid in a flask makes L moles and the liquid has a composition x_i ($i = 1, 2, \dots n$). After the evaporation of a small amount of liquid ΔL , vapor with a composition y_i ($i = 1, 2, \dots n$), will be formed which represents an equilibrium of the remaining liquid, the amount of which is equal to $L - \Delta L$ moles and the composition is $x_i + \Delta x_i$.

The material balance for i component is:

$$Lx_i = (\Delta L)y_i + (L - \Delta L)(x_i + \Delta x_i) \quad (1.9)$$

In limit at $\Delta L \rightarrow 0$,

$$Ldx_i/dL = x_i - y_i \quad (1.10)$$

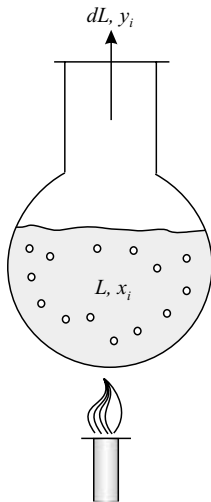


Figure 1.3. Open evaporation process (open distillation). x, y , composition of liquid and equilibrium vapor phases; L , amount of liquid; dL , infinitesimal amount of evaporated liquid.

Denoting $dt = dL/L$, we will get the equation of a residue curve:

$$dx_i/dt = x_i - y_i \quad (i = 1, 2, \dots, n) \quad (1.11)$$

The residue curve represents the change in a mixture composition during the open evaporation process. Each point of this line corresponds to a certain moment of time and to a portion of evaporated liquid.

From Eq. (1.11), it results that in each point of a residue curve a liquid–vapor tie-line is tangent to this line. The residue curves are convenient for the description of phase equilibrium because as these lines are continuous and noncrossing.

These lines were used for the first time to describe phase behavior of three-component azeotropic mixtures at the beginning of the twentieth century (Ostwald, 1900; Schreinemakers, 1901). Later, the residue curves of three-component azeotropic mixtures were studied in the works of Reinders & De Minjer (1940a, 1940b) for the azeotropic mixture acetone–chloroform–benzene and more widely in the works by Bushmakin & Kish (1957a, 1957b). Gurikov (1958) developed the first classification of three-component mixtures residue curve diagrams. In the works of Zharov (1967, 1968a, 1968b) and Serafimov (1969) the residue curve diagrams analysis and classification were applied for four-component and multicomponent mixtures. Several years later, these works were summarized in a monograph by Zharov & Serafimov (1975). In recent years, other versions of residue curve diagram classifications were developed (Matsuyama & Nishimura, 1977; Doherty & Caldarola, 1985).

Points of pure components and azeotropes are *stationary or singular points of residue curve bundles*. At these points, the value dx_i/dt in Eq. (1.11) becomes equal to zero. A stationary point at which all residue curves come to an end is called a *stable node* (the temperature increases in the direction of this point). A specific point at which all residue curves start is called an *unstable node* (the temperature

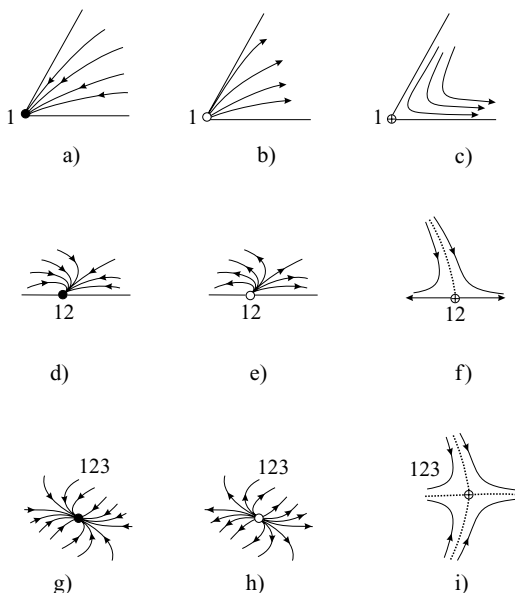


Figure 1.4. Types of stationary points of three-component mixtures: (a) one-component stable node, (b) one-component unstable node, (c) one-component saddle, (d) two-component stable node, (e) two-component unstable node, (f) two-component saddle, (g) three-component stable node, (h) three-component unstable node, and (i) three-component saddle. Arrows, direction of residium curves.

increases in the opposite direction of this point). The rest of stationary points are called *saddles* (Fig. 1.4).

A stationary point type is defined by the *proper values* of Yakobian from Eq. (1.11). For a stable node, both proper values are negative, $\lambda_1 < 0$ and $\lambda_2 < 0$; for an unstable node, both proper values are positive, $\lambda_1 > 0$ and $\lambda_2 > 0$; and for a saddle, one proper value is negative, $\lambda_1 < 0$, and the second is positive, $\lambda_2 > 0$.

For a distillation process not only the stationary point type, but also the behavior of the residue curve in the vicinity of the stationary point is of special importance. If the residue curves in the vicinity of the specific point are tangent to any straight line (singular line) (Fig. 1.4a, b, d, e, g, h), the location of this straight line is of great importance. A special point type and behavior of residue curves in its vicinity are called stationary point *local characteristics*.

The whole concentration space can be filled with one or more residue curve bundles. Each residue curve bundle has its own initial point (unstable node) and its own final point (stable node). Various bundles differ from each other by initial or final points.

The boundaries separating one bundle from another are specific residue curves that are called the *separatrixes of saddle stationary points*. In contrast to the other residue curves, the separatrixes begin or come to an end, not in the node points but in the saddle points. A characteristic feature of a separatrix is that in any vicinity of its every point, no matter how small it is, there are points belonging to two different bundles of residue curves. The concentration space for ideal mixtures is filled with one bundle of residue curves. Various types of azeotropic mixtures differ from each other by a set of stationary points of various types and by the various sequence of boiling temperatures in the stationary points.

The first topological equation that connects a possible number of stationary points of various types for three-component mixtures (N , node; S , saddle; upper index is the number of components in a stationary point) was deduced (Gurikov, 1958):

$$2(N^3 - S^3) + N^2 - S^2 + N^1 = 2 \quad (1.12)$$

Figure 1.5 shows mainly physically valuable *types of three-component azeotropic mixtures* deduced by Gurikov (1958) by means of systematic application of Eq. (1.12). In Fig. 1.5, one and the same structure cover a certain type of mixture and an antipodal type in which stable nodes are replaced by unstable ones and vice versa (i.e., the direction of residue curves is opposite). Besides that, the separatrixes are shown by the straight lines. Let's note that the later classifications of three-component mixture types (Matsuyama & Nishimura, 1977; Doherty & Caldarola, 1985) contain considerably greater number of types, but many of these types are not different in principle because these classifications assume light, medium, and heavy volatile components to be the fixed vertexes of the concentration triangle.

Types of azeotropic mixture and separatrixes arrangements are also called mixture *nonlocal characteristics*.

The part of the concentration space filled with one residue curve bundle is called a *distillation region* Reg^∞ (Schreinemakers, 1901). A distillation region $\text{Reg}_{(3)}^\infty$ has

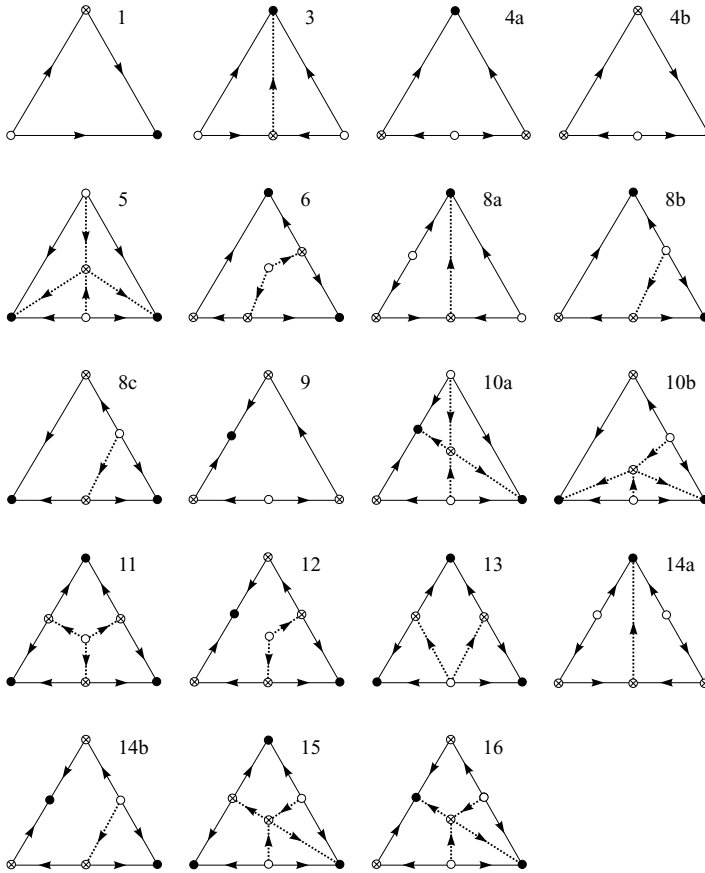


Figure 1.5. Types of three-component mixtures according to Gurikov (1958). Arrows, direction of residuum curves (bonds); dotted lines, separatrixes.

boundary elements that include the separatrices, segments of the concentration triangle sides $\text{Reg}_{(2)}^\infty$, and stationary points $\text{Reg}_{(1)}^\infty$ referring to this region. A distillation region of a three-component mixture $\text{Reg}_{(3)}^\infty$ is *two-dimensional*; separatrices, and segments of the concentration triangle sides $\text{Reg}_{(2)}^\infty$ are *one-dimensional*; and stationary points $\text{Reg}_{(1)}^\infty$ have *zero dimensionality*. Distillation regions and their boundary elements are also called concentration space *structural elements*.

Besides these structural elements, concentration space has other structural elements that are of great importance for a distillation process under various modes.

1.5. Residue Curve Bundles of Four-Component Mixtures

The structure of residue curve bundles of four-component mixtures is significantly more complex and diverse than that of three-component mixtures. This is due to the fact that each four-component mixture consists of four three-component constituents. Therefore, the number of types of four-component mixtures is enormous. In addition to that, four-component mixtures can have four-component node and saddle azeotropes. In contrast to three-component mixtures, the enormous

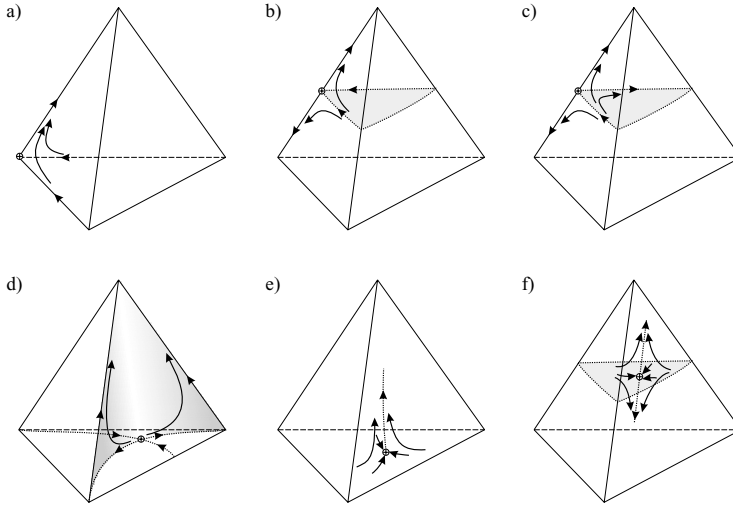


Figure 1.6. Types of saddle points of four-component mixtures: (a) one-component saddle, (b, c) two-component saddle, (d, e) three-component saddle, and (f) four-component saddle. Separatrix surfaces are shaded. Arrows, direction of residuum curves; dotted lines, separatrices.

number of four-component mixture structures makes their overall sorting out practically impossible. However, a topological equation for four-component mixtures similar to Eq. (1.12) was obtained (Zharov & Serafimov, 1975).

To understand the peculiarities of location of residue curve bundles of four-component mixtures, let's consider their behavior in the vicinity of saddle points (Fig. 1.6) and the nonlocal characteristics of the residue curve bundles using separate examples of the four-component mixture structures (Fig. 1.7). In Fig. 1.7, the *separating surfaces* of the residue curve bundles representing the *two-dimensional bundles* $\text{Reg}_{(3)}^\infty$ are shaded. Considering the nonlocal characteristics of the residue curve bundles, the simplest of such characteristics refers to each pair of stationary points. A pair of stationary points can be connected or not connected by the residue curve. To be brief, let's call the line of distillation that connects a pair of stationary points a *bond* (link) – it will be designated by the arrow (\rightarrow) that is directed toward the side of the temperature increase (Petlyuk, Kievskii, & Serafimov, 1975a, 1975b, 1977, 1979). For example, in Fig. 1.7a, $12 \rightarrow 23$. In the same figure, points 1 and 2 are not bonded.

The totality of all bonds characterizes the mixture's structure. The bond serves as the *elementary nonlocal characteristic* of the residue curve bundle structure. Bonds form bond chains. The *bond chains* of maximum length connect the unstable node N^- and the stable node N^+ of the distillation region Reg^∞ . Let's call a polyhedron formed by all stationary points of one maximum-length bond chain and containing all components of the mixture a *distillation subregion* Reg_{sub} .

The distillation region Reg^∞ is a polyhedron formed by all stationary points of the totality of all maximum-length bond chains connecting the same unstable node of the composition space with the same stable node (it will be designated \Rightarrow). The examples of distillation regions Reg^∞ are $12 \Rightarrow 4$, $12 \Rightarrow 2$ (at Fig. 1.7a),

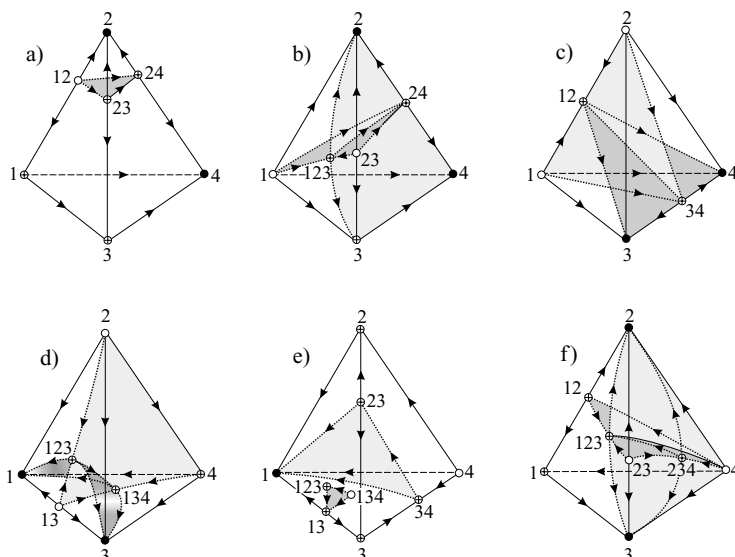


Figure 1.7. The examples of four-component structures (bonds and distillation regions Reg^∞). Separatrix surfaces are shaded. Arrows, direction of residuum curves; dotted lines, separatrixes.

$1 \Rightarrow 4, 1 \Rightarrow 2, 23 \Rightarrow 4, 23 \Rightarrow 2$ (at Fig. 1.7b), $1 \Rightarrow 3, 1 \Rightarrow 4, 2 \Rightarrow 3, 2 \Rightarrow 4$ (at Fig. 1.7c), $13 \Rightarrow 1, 13 \Rightarrow 3, 2 \Rightarrow 1, 2 \Rightarrow 3$ (at Fig. 1.7d), $134 \Rightarrow 1, 4 \Rightarrow 1$ (at Fig. 1.7e), $23 \Rightarrow 2, 23 \Rightarrow 3, 4 \Rightarrow 2$, and $4 \Rightarrow 3$ (at Fig. 1.7f).

The examples of distillation subregions Reg_{sub} are $12 \rightarrow 23 \rightarrow 3 \rightarrow 4$, $12 \rightarrow 1 \rightarrow 3 \rightarrow 4$, and $12 \rightarrow 23 \rightarrow 24 \rightarrow 4$ (Fig. 1.7a). In this case, the distillation region Reg^∞ is $12 \Rightarrow 4$ ($\text{Reg}_{\text{sub}} \in \text{Reg}^\infty$), or

$$\begin{array}{ccccccc}
 \uparrow & \rightarrow & 1 & \rightarrow & \downarrow \\
 12 & \rightarrow & 23 & \rightarrow & 3 & \rightarrow & 4 \\
 & & \downarrow & \rightarrow & 24 & \rightarrow & \uparrow
 \end{array}$$

As we will see in Chapter 3, the distillation region and subregion characterize those possible product compositions that can be produced from the given feedstock composition by distillation under one of the most important modes, in particular, under the *infinite reflux mode*.

A bond, bond chain, distillation subregion, and region are the nonlocal structural elements of the azeotropic mixture concentration space.

1.6. Matrix Description of the Multicomponent Mixture Residue Curve Structure

The structure of the residue curve bundles can be obviously represented only for binary, three-, and four-component mixtures. For mixtures with more components, it is impossible. However, practice needs make necessary the analysis of the bundle structure with any number of components. This problem can be solved by means of a structure matrix description (Petlyuk et al., 1975a, 1975b).

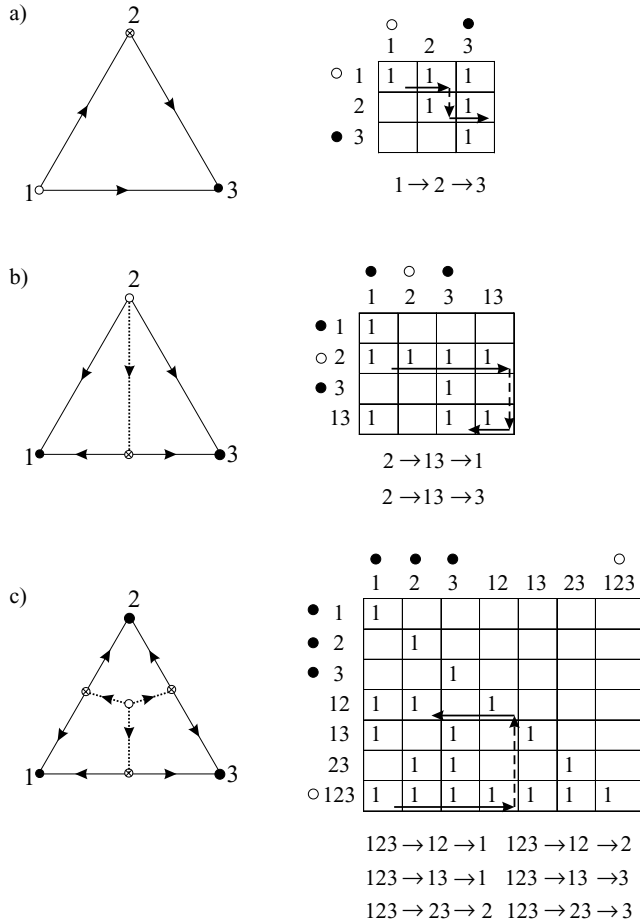


Figure 1.8. The examples of three-component structures and their structural matrices. Arrows, direction of residuum curves; dotted lines, separatrix; thick line with arrow, bond; dotty lines, transfer to next bond.

By the *structural matrix* of the azeotropic mixture concentration space, we will name a square matrix, the columns and lines of which correspond to the stationary points and the elements of which $a_{ij} = 1$, if there is a bond directed from stationary point i to stationary point j ($a_{ij} = 0$, if such a bond is missing). For the purpose of obviousness, some examples of three-component mixture structural matrices are shown in Fig. 1.8.

Each line of a structural matrix corresponds to the i th stationary point and each column to the j th one. Diagonal elements $a_{ij} = 1$ (it is accepted conditionally that each specific point is bonded to itself). The components are labeled 1, 2, 3; binary azeotropes are designated by two-digit numbers, 12, 13, 23; and the ternary azeotrope by a three-digit number, 123. Zero column corresponds to an unstable node N^- and zero line to the stable N^+ one (except for the diagonal elements). Structural matrices provide an opportunity to easily single out all maximum-length

bond chains (i.e., all the distillation subregions). For example, in Fig. 1.8c, the distillation subregions Reg_{sub} are as follows: $123 \rightarrow 12 \rightarrow 1$, $123 \rightarrow 13 \rightarrow 1$, $123 \rightarrow 12 \rightarrow 2$, $123 \rightarrow 23 \rightarrow 2$, $123 \rightarrow 23 \rightarrow 3$, and $123 \rightarrow 13 \rightarrow 3$. Respectively, the distillation regions Reg_{∞} are as follows: $123 \Rightarrow 1$, $123 \Rightarrow 2$, $123 \Rightarrow 3$, or

$$\begin{array}{ccccccc} \uparrow & \rightarrow & 13 & \rightarrow & \downarrow, & \uparrow & \rightarrow & 23 & \rightarrow & \downarrow, & \uparrow & \rightarrow & 13 & \rightarrow & \downarrow \\ 123 & \rightarrow & 12 & \rightarrow & 1 & 123 & \rightarrow & 12 & \rightarrow & 2 & 123 & \rightarrow & 23 & \rightarrow & 3 \end{array}$$

1.7. Lines, Surfaces, and Hypersurfaces $K_i = K_j$

In Sections 1.3 to 1.5, the residue curve bundles, which characterize the direction of liquid–vapor tie-lines in each point of the concentration space (i.e., the phase equilibrium field), were considered. As stated previously, such characteristics of the phase equilibrium field and structural elements related to it (bonds, distillation regions, and subregions) are the most important for one of the distillation modes, in particular, for the infinite reflux mode.

However, the liquid–vapor phase equilibrium field has other important characteristics that become apparent under other distillation modes, in particular, under *reversible distillation* and usual (adiabatic) *distillation with finite reflux*.

To such characteristics are referred, first of all, lines, surfaces, and hypersurfaces of the phase equilibrium coefficients equality ($K_i = K_j$). For the purpose of brevity, we will name these lines, surfaces, and hypersurfaces as α -lines, α -surfaces, and α -hypersurfaces (or *univolatility lines, surfaces, and hypersurfaces*: $\alpha_{ij} = K_i / K_j = 1$).

Univolatility α -lines, α -surfaces, and α -hypersurfaces divide the concentration simplex into *regions of order of components* Reg_{ord} (in Reg_{ord} $K_i > K_j > K_k$) (Petlyuk & Serafimov, 1983).

The totality of several regions of components' order for which one and the same component appear to be the most light volatile ($K_l = \max K_i$) or the most heavy volatile ($K_h = \min K_i$) was named as a *region of reversible distillation* $\text{Reg}_{\text{rev}, s}^l$ or $\text{Reg}_{\text{rev}, r}^h$ (Petlyuk, 1978). Such a name can be explained by the crucial meaning of these regions for possibly realizing of reversible distillation (see Chapter 4).

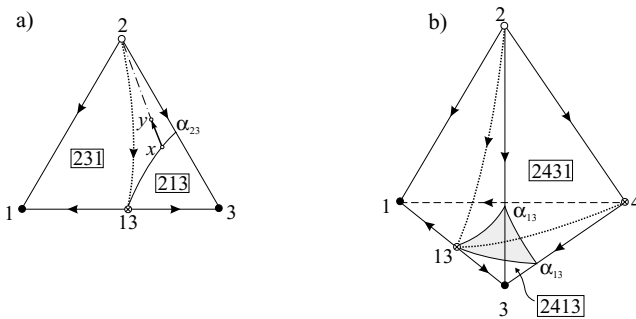


Figure 1.9. α -lines, α -surfaces (shaded), and regions of order of components Reg_{ord} for (a) three-component and (b) four-component mixtures. 231 , 213 , 2431 , and 2413 , regions of component order Reg_{ord} , Reg_{ord} , Reg_{ord} , and Reg_{ord} ; $x \rightarrow y$, tie-line liquid–vapor for point x on α -line; arrows, direction of residuum curves; dotted lines, separatrixes.